Lubricating oils

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Uittreksel

A base lubricating oil composition comprising: (a) a base oil having a viscosity index of at least 94 obtained by hydrotreating a solvent-extracted raffinate having a viscosity index of at most 92, and (b) a solvent-extracted raffinate having a viscosity index of at most 92, and/or a deasphalted vacuum residue and/or a hydrotreated deasphalted vacuum residue, shows improved oxidation stability.

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(54) Lubricating oils

(57) A base lubricating oil composition comprising:

(a) a base oil having a viscosity index of at least 94 obtained by hydrotreating a solvent-extracted raffinate having a viscosity index of at most 92, and

(b) a solvent-extracted raffinate having a viscosity index of at most 92, and/or a deasphalted vacuum residue and/or a hydrotreated deasphalted vacuum residue, shows improved oxidation stability.

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SPECIFICATION
Oil compositions

The invention is concerned with improving the oxidation stability of certain base oils.

Base oil, e.g. lubricating oils, transmission fluids or industrial oils, are prepared from various petroleum feedstocks, e.g. vacuum distillates or deasphalted vacuum residues or mixtures thereof. One important class of base oil is those base oils having a viscosity index (V.I.) of at least 94. Since most feedstocks have a V.I. of below 94, e.g. of from 20 to 85, it is important to subject such feedstocks to a processing step which increases the V.I. thereof to at least 94.

It is possible to increase the V.I. of a feedstock by solvent extraction alone or by hydrotreating alone or by both solvent extraction and hydrotreating. The present invention is particularly concerned with those base oils prepared by both solvent extraction of the feedstock, e.g. to an extent such that the solvent-extracted raffinate has a V.I. of at most 92, and hydrotreating the solvent-extracted raffinate, e.g. to an extent such that the resultant base oil has a V.I. of at least 94. One characteristic of such base oils is that they sometimes darken and/or form sludge when exposed to oxygen. This phenomenon is usually described as oxidation instability.

It has now been found that the oxidation stability of such base oils is improved by the addition thereto of a solvent-extracted raffinate having a viscosity index of at most 92 and/or by the addition of a deasphalted vacuum residue and/or a hydrotreated deasphalted vacuum residue.

Accordingly, the present invention is concerned with a base oil composition comprising:

(a) a base oil having a viscosity index of at least 94 obtained by hydrotreating a solvent-extracted raffinate having a viscosity index of at most 92, and

(b) a solvent-extracted raffinate having a viscosity index of at most 92, and/or a deasphalted vacuum residue and/or a hydrotreated deasphalted vacuum residue.

The base oil of the base oil composition may be prepared from any suitable petroleum feedstock. As stated above the V.I. of such feedstocks is usually from 20 to 85. Examples of suitable feedstocks include vacuum distillates, deasphalted residues of vacuum distillations (deasphalted vacuum residues) and mixtures thereof derived from crude oils, e.g. paraffinic crude oils. Distillate feedstocks usually have a V.I. of from 20 to 60 and residual feedstocks usually have a V.I. of from 60 to 85.

Such feedstocks are then solvent-extracted to increase the V.I. Preferably, the V.I. of the solvent-extracted raffinate is from 75 to 92. In the case of a feedstock already having a V.I. of above 75 it is desirable that it is solvent-extracted to an extent such that the V.I. of the raffinate is at least 5 V.I. units above the V.I. of the feedstock. Solvent extraction is a well known technique and suitable solvents include phenol, furfural or sulphur dioxide. After extraction an aromatic extract and a solvent-extracted raffinate are obtained.

The solvent-extracted raffinate is then hydrotreated to an extent such that the resultant base oil has a V.I. of at least 94, suitably of from 95 to 110, although the V.I. of the resultant base oil may be as high as 120 or higher, e.g. above 140 (extra-high V.I. base oil). Hydrotreating is a well known technique and usually comprises treating the raffinate with hydrogen at a temperature of from 350°C to 500°C, a pressure of from 60 to 200 bars in the presence of a catalyst using space velocities of from 0.1 to 2.0 kg feed per litre catalyst per hour. Suitable catalysts usually comprise one or more of the metals molybdenum, chromium, tungsten, vanadium, platinum, nickel, copper, iron and cobalt or their oxides and/or sulphides, either supported on a suitable carrier, such as alumina or silica or unsupported. Particularly advantageous catalysts are the iron transition metals (iron, cobalt and nickel) and the Group VIB metals (chromium, molybdenum and tungsten) especially combinations of metals from each of these groups, for instance cobalt and molybdenum, nickel and tungsten, and nickel and molybdenum supported on alumina. The catalyst may also contain promoters, such as compounds containing phosphorus, fluorine or borium. Usually the V.I. of the solvent-extracted raffinate is increased by at least 5 V.I. units by the hydrotreatment.

It is preferred to add a solvent-extracted raffinate having a viscosity index of at most 92 to the base oil. Suitable amounts of such raffinates are from 0.1 to 20%w, preferably from 0.1 to 10%w based on the weight of the base oil. Suitable solvent-extracted raffinates having a viscosity index of at most 92 are those prepared as described above for the preparation of the base oil. The petroleum feedstocks, from which such raffinates may be prepared may be vacuum distillates, deasphalted vacuum distillates or mixtures thereof. Various combinations are possible, e.g. a solvent-extracted raffinate derived from a deasphalted vacuum residue may be added to a base oil derived from a vacuum distillate or from a deasphalted vacuum residue; and a solvent-extracted raffinate derived from a vacuum distillate may be added to a base oil derived from a deasphalted vacuum residue or from a vacuum distillate.

The base oil from which the compositions of the present invention are obtained may be, or may have been, subjected to one or more additional processing steps, such as a finishing step and/or a distillation step and/or a dewaxing step. The base oil may be subjected to a distillation step in order to remove the more volatile components therefrom. For example the volatile material boiling below a temperature in the range of from 200 to 550°C may be removed. Dewaxing serves to decrease the pour

point of the feedstocks by removing wax therefrom and is usually carried out after the hydrotreatment step. Finishing steps include clay and/or acid treatments and/or hydrofinishing treatment.

In addition, the solvent-extracted raffinate, which is preferably added to the base oil, may be, or may have been, subjected to one or more processing steps, such as a dewaxing step. The raffinate may be dewaxed in admixture with the base oil.

The base oil compositions of the present invention are suitably used as lubricating oil compositions for internal combustion engines and may contain one or more conventional additives, such as viscosity index improvers, anti-wear/extreme-pressure additives, detergents, anti-rust additives, pour point depressants and other anti-oxidants, e.g. secondary amines, and/or other daylight stabilizers, such as quinones (e.g. tetrabutyldiphenolquinone).

The invention will now be illustrated by reference to the following Examples. In the Examples the V.I.'s and viscosities were determined on dewaxed samples.

EXAMPLES 1, 2 and 3

A base oil was prepared by extracting a vacuum distillate (derived from a light paraffinic crude oil) having a V.I. of 54.5 and a viscosity of 5.03 centistokes at 98.9°C. The extractant used was furfural and the solvent-extracted raffinate had a V.I. of 87. The raffinate thus obtained was treated with hydrogen, using a Ni/W alumina supported catalyst, at a temperature of 361°C, a pressure of 90 bar and a space velocity of 1.5 kg feed per litre catalyst per hour. The hydrotreated base oil was then distilled to remove components having a boiling point of below about 365°C and dewaxed with a mixture (50/50) of methylethylketone (MEK) and toluene. The V.I. and viscosity of the dewaxed and distilled hydrotreated base oil was 95 and 4.27 centistokes at 98.9°C respectively.

The final base oil was subjected to an oxidation stability test. This test comprised blowing air through the base oil at a temperature of 160°C for 168 hours, at the end of the test the amount of sludge formed, the acidity and the viscosity increase of the base oil were determined. The results (Example (a)) are given in Table I.

Base oil compositions according to the present invention were then prepared by adding various amounts of a solvent-extracted raffinate having a V.I. of 88 and a viscosity of 40.8 centistokes at 98.9°C. The raffinate was prepared by extracting a deasphalted vacuum residue (derived from a light paraffinic crude oil) having a V.I. of 66 and a viscosity of 56.9 centistokes at 98.9°C with furfural followed by dewaxing with a mixture (50/50) of MEK and toluene. The base oil compositions obtained were subjected to the oxidation stability test as described above. The results (Examples (1) and (2)) are also given in Table I.

Another base oil composition according to the present invention was prepared by replacing the solvent-extracted raffinate with the deasphalted vacuum residue, after dewaxing as described above, from which it was prepared. The base oil composition was also subjected to the oxidation stability test as described above. The results (Example (3)) are also given in Table I.

TABLE I

Example	Additive (%w) on base oil		Oxidation stability		
	solvent extracted raffinate	deasphalted vacuum residue	sludge, %w on composition	acidity, mg eq./100 g	viscosity increase %
(a)	—	—	10	30	510
1	2	—	0.77	3.2	24
2	5	—	—	—	—
3	—	2	0.9	3.4	26

EXAMPLE 4

Example 2 was repeated with the differences that the vacuum distillate, from which the base oil was prepared, had a V.I. of 29 and a viscosity of 18.0 centistokes at 98.9°C, that the solvent-extracted raffinate had a V.I. of 88 and a viscosity of 12.2 centistokes at 98.9°C and that the base oil, after hydrotreatment, had a V.I. of 97 and a viscosity of 10.5 centistokes at 98.9°C. The solvent-extracted raffinate added thereto was as described for Example 2. The base oil (Example (b)) and the base oil composition were subjected to the oxidation stability test as described above. The results are given in Table II.

TABLE II

Example	Additive (%w) on base oil	Oxidation stability		
		sludge, %w on composition	acidity, mg eq./100 g	viscosity increase %
(b)	–	0.05	26	360
4	5	0.05	1.4	17

EXAMPLES 5 and 6

A base oil was prepared by extracting a vacuum distillate (derived from a paraffinic crude oil) having a V.I. of 48 and a viscosity of 17.6 centistokes at 98.9°C. The extractant used was furfural and the solvent-extracted raffinate had a V.I. of 82 and a viscosity of 13.5 centistokes at 98.9°C. The solvent-extracted raffinate was hydrotreated, distilled and dewaxed as described in Examples 1 and 2 and the V.I. and viscosity of the dewaxed and distilled hydrotreated base oil was 96 and 10.15 centistokes at 98.9°C, respectively. This base oil (Example (c)) was then subjected to the oxidation stability test as described above.

Base oil compositions according to the present invention were then prepared by adding to the base oil various amounts of the solvent-extracted raffinate having a V.I. of 82 and a viscosity of 13.5 centistokes at 98.9°C after dewaxing with a mixture (50/50) of MEK and toluene, and also subjected to the oxidation stability test. The results are given in Table III.

TABLE III

Example	Additive (%w) on base oil	Oxidation stability		
		sludge, %w on composition	acidity, mg eq./100 g	viscosity increase %
(c)	–	nil	14.9	94
5	0.5	nil	3.6	15
6	3.0	nil	1.7	7.7

CLAIMS

1. A base oil composition comprising:

(a) a base oil having a viscosity index of at least 94 obtained by hydrotreating a solvent-extracted raffinate having a viscosity index of at most 92, and

(b) a solvent-extracted raffinate having a viscosity index of at most 92, and/or a deasphalted vacuum residue and/or a hydrotreated deasphalted vacuum residue.

2. A composition as claimed in claim 1, wherein the amount of (b) is from 0.1 to 20%w, based on the weight of (a).

3. A composition as claimed in claim 1 or claim 2, wherein (a) is derived from a vacuum distillate and/or deasphalted vacuum residue.

4. A composition as claimed in any one of claims 1 to 3, wherein (a) is obtained by hydrotreating a solvent-extracted raffinate having a viscosity index of from 75 to 92.

5. A composition as claimed in any one of claims 1 to 4, wherein (b) is a solvent-extracted raffinate having a viscosity index of from 75 to 92.

6. A composition as claimed in any one of claims 1 to 5, wherein (a) has been subjected to a finishing step and/or a distillation step and/or a dewaxing step.

7. A composition as claimed in any one of claims 1 to 6, wherein (b) has been subjected to a dewaxing step.

8. A composition as claimed in claim 1, substantially as hereinbefore described with particular reference to the Examples.

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(54) Basisoliecomposities.

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verschillende hoeveelheden van een door oplosmiddelextractie verkregen raffinaat met een viscositeitsindex van 88 en een viscositeit van 40,8 cS bij 98,9°C. Het raffinaat werd bereid door een ontasfalteerd vacuümresidu (afkomstig van een lichte paraffinehoudende ruwe olie) met een viscositeitsindex van 66 en een viscositeit van 56,9 cS bij 98,9°C met furfural te extraheren, waarna het met een mengsel (50/50) van MEK en tolueen werd ontparaffineerd. De verkregen basisoliecomposities werden aan de hierboven beschreven oxydatiebestendigheidsproef onderworpen. De resultaten (Voorbeelden 1 en 2) zijn eveneens in Tabel I vermeld.

Een andere basisoliecompositie volgens de onderhavige uitvinding werd bereid door het door oplosmiddelextractie verkregen raffinaat te vervangen door het ontasfalteerde vacuümresidu waaruit het was bereid, nadat bovengenoemde ontparaffinering was toegepast. De basisoliecompositie werd ook aan bovengenoemde oxydatiebestendigheidsproef onderworpen. De resultaten (Voorbeeld 3) zijn eveneens in Tabel I vermeld.

TABEL I

Voorbeeld	Toevoegsel (gew.%), berekend op basisolie		Oxydatiebestendigheid		
	door oplosmiddel extractie verkregen raffinaat	ontasfalteerd vacuüm-residu	drab, gew.%, berekend op compositie	zuurgraad mg eq./100g	verhoging van viscositeit %
(a)	–	–	10	30	510
1	2	–	0,77	3,2	24
2	5	–	–	–	–
3	–	2	0,9	3,4	26

Voorbeeld 4

Voorbeeld 2 werd herhaald, doch thans had het vacuümdestillaat waaruit de basisolie werd bereid, een viscositeitsindex van 29 en een viscositeit van 18,0 cS bij 98,9°C, had het door oplosmiddelextractie verkregen raffinaat een viscositeitsindex van 88 en een viscositeit van 12,2 cS bij 98,9°C en had de basisolie na hydrogenering een viscositeitsindex van 97 en een viscositeit van 10,5 cS bij 98,9°C. Het eraan toegevoegde, door oplosmiddelextractie verkregen raffinaat was zoals beschreven onder Voorbeeld 2. De basisolie (Voorbeeld b) en de basisoliecompositie werden aan bovengenoemde oxydatiebestendigheidsproef onderworpen. De resultaten zijn in tabel II vermeld.

TABEL II

Voorbeeld	Toevoegsel (gew.%), berekend op basisolie	Oxydatiebestendigheid		
		drab, gew.%, berekend op compositie	zuurgraad, mg eq./100 g	verhoging van viscositeit
(b)	–	0,05	26	360
4	5	0,05	1,4	17

Voorbeelden 5 en 6

Een basisolie werd bereid door extractie van een vacuümdestillaat (afkomstig van een paraffinehoudende ruwe olie) met een viscositeitsindex van 48 en een viscositeit van 17,6 cS bij 98,9°C. Het gebruikte extractiemiddel van furfural en het door oplosmiddelextractie verkregen raffinaat had een viscositeitsindex van 82 en een viscositeit van 13,5 cS bij 98,9°C. Het door oplosmiddelextractie verkregen raffinaat werd

gehydrogeneerd, gedestilleerd en ontparaffineerd, zoals beschreven in Voorbeelden 1 en 2, en de viscositeitsindex en de viscositeit van de ontparaffineerde en gedestilleerde, gehydrogeneerde basisolie waren respectievelijk 96 en 10,15 cS bij 98,9°C. Deze basisolie (Voorbeeld c) werd vervolgens aan bovengenoemde oxydatiebestendigheidsproef onderworpen.

Basisoliecomposities volgens de onderhavige uitvinding werden vervolgens bereid door aan de basisolie verschillende hoeveelheden toe te voegen van het door oplosmiddelextractie verkregen raffinaat met een viscositeitsindex van 82 en een viscositeit van 13,5 cS bij 98,9°C, na ontparaffinering met een mengsel (50/50) van MEK en tolueen. De composities werden eveneens aan de oxydatiebestendigheidsproef onderworpen. De resultaten zijn in Tabel III vermeld.

TABEL III

Voorbeeld	Toevoegsel (gew.%), berekend op basisolie	Oxydatiebestendigheid		
		drab, gew.%, berekend op compositie	zuurgraad, mg eq./100 g	verhoging van viscositeit %
(c)	–	nihil	14,9	94
5	0,5	nihil	3,6	15
6	3,0	nihil	1,7	7,7

Conclusies

1. Een basisoliecompositie, met het kenmerk, dat deze bevat:
a. een basisolie met een viscositeitsindex van ten minste 94, die is bereid door hydrogenering van een door oplosmiddelextractie verkregen raffinaat met een viscositeitsindex van ten hoogste 92, en b. een door oplosmiddelextractie verkregen raffinaat met een viscositeitsindex van ten hoogste 92 en/of een ontasfalteerd vacuümresidu, waarbij de hoeveelheid van b. 0,1–20 gew.% is, berekend op het gewicht van a.

2. Compositie volgens conclusies 1, met het kenmerk, dat a. van een vacuümdestillaat en/of ontasfalteerd vacuümresidu wordt afgeleid.

3. Compositie volgens een der conclusies 1 of 2, met het kenmerk, dat a. wordt bereid door hydrogenering van een door oplosmiddelextractie verkregen raffinaat met een viscositeitsindex van 75–92.

4. Compositie volgens een der conclusies 1–3, met het kenmerk, dat b. een door oplosmiddelextractie verkregen raffinaat is dat een viscositeitsindex tussen 75 en 92 heeft.

5. Compositie volgens een der conclusies 1–4, met het kenmerk, dat a. aan een eindbehandeling en/of destillatie en/of ontparaffinering is onderworpen.

6. Compositie volgens een der conclusies 1–5, met het kenmerk, dat b. is ontparaffineerd.